

Dyeing of nylon with reactive dyes. Part 1. The effect of changes in dye structure on the dyeing of nylon with reactive dyes

A. Soleimani-Gorgani, J.A. Taylor*

*Textiles and Paper, School of Materials, University of Manchester, PO Box 88, Sackville Street,
Manchester M60 1QD, UK*

Received 13 January 2005; accepted 25 January 2005
Available online 25 March 2005

Abstract

The dyeing behaviour of seven red commercial cellulosic reactive dyes, all based on the same chromophore and possessing one or more reactive group, and one to three chromophore units, were evaluated on nylon. Fixation levels appeared to be independent of the number of either reactive groups or chromophore units. Also, the degree of sulphonation, per se, appeared to have little effect on fixation, whereas the type of reactive group was important. The major determinant of dye fixation appeared to be associated with the shape of the molecule and the type, not the number, of reactive groups.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Reactive dyes; Nylon; Molecular size; Fixation efficiency

1. Introduction

The presence of terminal amino end groups in nylon fibres imparts substantivity towards anionic dyes, specifically acid dyes, direct dyes and reactive dyes. Acid dyes are commonly used on nylon, with 1:2 pre-metallised acid dyes generally being used when reasonable levels of wet fastness [1] are required. However, even these dyeings can cause some staining of adjacent fabrics during laundering. Whilst an after-treatment of the dyed nylon can result in somewhat improved wet-fastness, repeated washing can still result in loss of colour and there remains much scope for improvement.

Reactive dyes for cellulose resemble acid dyes in their basic structure, but additionally possess one or more fibre reactive group, their name being derived from their ability to react chemically with groups on the fibre. In

the mid-fifties Rattee and Stephen [2–5] showed that dyes containing a dichlorotriazinyl reactive group are capable of reacting with cellulosic fibres, in the presence of alkali, to form covalent dye to fibre bonds. Subsequently, research into the chemistry and the application of reactive dyes focused overwhelmingly on cellulosic fibres [6,7]. In contrast, considerably less attention has centred on reactive dyes for polyamide fibres. Thus, compared with the vast number of reactive dyes for cellulose [8], relatively few reactive dyes have been introduced specifically for polyamide fibres. It is known that some reactive dyes, which were developed for cellulosic fibres, can be covalently fixed at the boil, to nylon at slightly acidic pH. Under these conditions, covalent bonds form between the dye and the amino groups of nylon, without the need for an alkaline fixation step [9,10]. Of the reactive dyes which have been developed specifically for application to nylon the Stanalan [11] and Eriofast [12] ranges are probably the best known. Eriofast dyes are metal-free, sulphonated reactive dyes, developed for application to nylon in order to achieve outstanding wet fastness properties.

* Corresponding author. Tel.: +44 161 200 4112; fax: +44 161 955 8150.

E-mail address: john.a.taylor@manchester.ac.uk (J.A. Taylor).

Water soluble dyes possessing electrophilic reactive groups such as chlorodifluoropyrimidines [13], bromoacrylamides [14], chlorotriazines and vinylsulphones [15,16], as well as some disperse types [17] have been evaluated on nylon.

As a first step towards the design of novel reactive dyes for nylon, and before embarking on a synthetic programme, an attempt was made to identify the structural features associated with good reactive dyeing performance on nylon. Therefore the effect, on dyeing properties, of changes in dye structure, including molecular size, number of reactive groups, type of reactive groups and also the degree of sulphonation were evaluated.

2. Experimental

2.1. Materials

Scoured, modified nylon 6.6 “*Tactel Coloursafe*” fabric was supplied by Du Pont (UK). Table 1 shows the commercial dyes selected. All were based on essentially the same chromophore. All Procion dyes were obtained from DyStar, Kayacelon React CN-3B was supplied by Nippon Kayaku and Drimarene Red P-4B was obtained from Clariant.

HyperChem version 7.5 was used for molecular modelling and three-dimensional analysis of molecules. HyperChem is available from Lightwave Scientific, UK.

3. Dyeing

Dyeings were carried out using a Roaches dyeing machine (Mathis Labomat BFA 12): 5 g pieces of fabric

were dyed at a liquor ratio of 20:1, using stainless steel dypots, each of 200 cm³ capacity. The dyeing method used is depicted in Fig. 1. At the end of the dyeing, the dyed fabric was removed and rinsed in cold tap water for 5 min. An initial series of dyeings was carried out at 1% dye o.m.f to determine the effect of pH on dyeing. Five different pH values were selected, pH values of, 2, 4, 6, and 8 were obtained by using McIlvaine buffers, as shown in Table 2 [18], pH 10 was achieved by adding sodium hydroxide to disodium hydrogen phosphate. No additional electrolyte, levelling agent or alkali was used. Subsequent dyeings were carried out on 5 g pieces of fabric, at eight depths of shade (0.05%, 0.1%, 0.2%, 0.5%, 0.8%, 1%, 1.5% and 2% o.m.f), at pH 4.

3.1. Colour strength (*K/S*) on fabric

Reflectance measurements on the dry dyed fabrics were carried out using a Datacolor Spectraflash 600 specrophotometer under a D65 lamp. The average of three reflectance measurements, taken at different positions on the dyed fabric, was used.

3.2. Dye exhaustion

The extent of dye exhaustion was determined spectrophotometrically. The absorbance of each dye-bath solution before and after the dyeing process was measured using 1 cm quartz cells housed in a Philips PU 8720 UV/visible scanning spectrophotometer at the λ_{\max} of each dye. The percentage dyebath exhaustion (%*E*) was calculated using Eq. (1), where A_0 and A_1 are the absorbance of the dyebath before and after dyeing, respectively.

$$\%E = \frac{A_0 - A_1}{A_0} \times 100 \quad (1)$$

Table 1
Commercial dyes used for dyeing, *Tactel Coloursafe*

| No. | Dye | No. of solubilising sulphonate groups | Reactive group type | No. of reactive groups |
|-----|---------------------------|---------------------------------------|-------------------------------|------------------------|
| D1 | Procion Red P-8B | 4 | MCT | 1 |
| D2 | Procion Red H-EXL | 3 | MCT | 1 |
| D3 | Drimarene Red P-4B | 3 | MCT | 1 |
| D4 | Procion Red H-E7B | 8 | MCT | 2 |
| D5 | Procion Red H-E3B | 6 | MCT | 2 |
| D6 | Kayacelon React Red CN-3B | 6 | 3-carboxypyridinium triazinyl | 2 |
| D7 | Procion Rubine XL + | 9 | MCT | 3 |

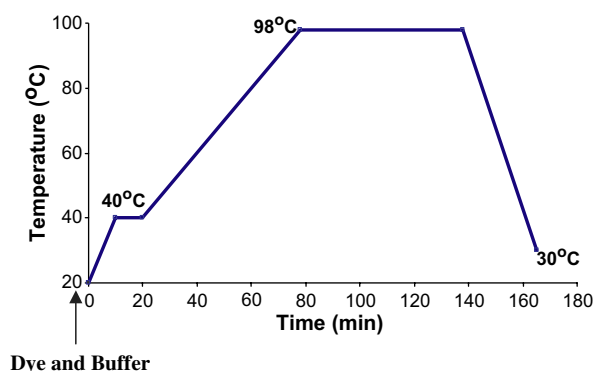


Fig. 1. Dyeing profile used.

Table 2
Composition of McIlvaine buffers in a total volume of 80 cm³

| pH | 0.2 M Na ₂ HPO ₄ (cm ³) | 0.1 M Citric acid (cm ³) |
|----|--|---|
| 2 | 1.6 | 78.4 |
| 4 | 30.9 | 49.1 |
| 6 | 50.6 | 29.4 |
| 8 | 77.8 | 2.2 |

3.3. Dye fixation

Only a proportion of the total dye present on the substrate reacts to form covalent linkages, whilst the remaining dye is attached by ionic bonds and by van der Waals forces. Therefore, in order to determine the degree of dye fixation, the following procedure was used.

A sample (1 g) of dyed fabric was immersed in 150 cm³ of 20% aqueous pyridine solution, the temperature was raised rapidly to boiling and treatment continued under reflux until no further dye was removed from the fibre, this took approximately 3 h. The stripped dyeing was thoroughly rinsed in tap water and allowed to dry in the open air. The extent of dye fixation was determined spectrophotometrically. The percentage fixation of the dye which exhausted, %*F*, was determined by a method used by several earlier workers [13–15] using Eq. (2) where (*K/S*)₁ and (*K/S*)₂ represent the colour strength of the dyeing before and after stripping of any unfixed colour with aqueous pyridine. This method assumes, at least at the concentration of dyes employed, that (*K/S*) values are proportional to concentration of dye on fibre. The overall percentage fixation, %*T*, was evaluated from Eq. (3)

$$\%F = \frac{(K/S)_2}{(K/S)_1} \times 100 \quad (2)$$

$$\%T = \frac{\%F \times \%E}{100} \quad (3)$$

3.4. Determination of effective agent content dyes

The effective agent content of the dyes were determined by titration against titanium (III) chloride [19].

4. Results and discussion

4.1. Effect of pH on dyeing performance

The ability of the amino groups in nylon to protonate at low pH effectively reduces the concentration of nucleophilic free amine and increases the affinity of

Table 3
(*K/S*)₁, (*K/S*)₂, %*E* and %*T* of dyes at the different pH values

| Dye | | pH | | | | |
|---------------------------|-----------------------------|------|------|-----|------|------|
| | | 2 | 4 | 6 | 8 | 10 |
| Drimarene Red P-4B | (<i>K/S</i>) ₁ | 11 | 8.8 | 4.1 | 1.3 | 0.2 |
| | (<i>K/S</i>) ₂ | 6.2 | 4.4 | 2.5 | 1.2 | — |
| | % <i>E</i> | 99 | 96 | 44 | 17 | 2 |
| | % <i>T</i> | 56 | 48 | 26 | 14 | — |
| Procion Red H-EXL | (<i>K/S</i>) ₁ | 10.2 | 11.3 | 8.5 | 1.8 | 0.2 |
| | (<i>K/S</i>) ₂ | 6 | 9.49 | 5.6 | 1.5 | — |
| | % <i>E</i> | 93 | 100 | 78 | 15 | 5 |
| | % <i>T</i> | 55 | 84 | 51 | 12.5 | — |
| Procion Red H-E3B | (<i>K/S</i>) ₁ | 9.9 | 8.9 | 5.2 | 0.6 | 0.2 |
| | (<i>K/S</i>) ₂ | 7.8 | 8.25 | 4.4 | 0.5 | — |
| | % <i>E</i> | 100 | 89 | 55 | 8 | 2 |
| | % <i>T</i> | 78 | 82.5 | 46 | 7 | — |
| Kayacelon React Red CN-3B | (<i>K/S</i>) ₁ | 1.3 | 2.7 | 0.6 | 0.12 | 0.07 |
| | (<i>K/S</i>) ₂ | 1.2 | 2.4 | 0.5 | — | — |
| | % <i>E</i> | 11.5 | 26 | 5 | 0.2 | 0.1 |
| | % <i>T</i> | 10 | 22 | 4.1 | — | — |
| Procion Rubine XL+ | (<i>K/S</i>) ₁ | 14.4 | 7.6 | 5 | 0.1 | 0.01 |
| | (<i>K/S</i>) ₂ | 4.5 | 4.75 | 2.8 | — | — |
| | % <i>E</i> | 90 | 48 | 30 | 0.63 | 0.1 |
| | % <i>T</i> | 28 | 30 | 17 | — | — |

anionic dyes for (cationic) nylon. The pH can therefore play an important role in determining the exhaustion and final fixation of reactive dyes on nylon. Therefore, before commencing a study of the influence of the dye chemistry on the dyeing of the modified nylon 6.6 “*Tactel Coloursafe*”, it was necessary to determine the optimum application pH. Dyeings were applied at several pH values. Buffers of pH 2, 4, 6, 8 and 10 were made up as described above and the dyes applied over 60 min at 98 °C.

As the results in Table 3 indicate the fixation of each of the five dyes, at 1% dye o.m.f, is highest in the pH range 2–4. The lowest total fixation for all the five dyes was achieved at pH 10. At high pH the nylon is essentially anionic (Fig. 2). Under these conditions, the concentration of nylon–NH₂, the active nucleophilic species, which reacts with the electrophilic group(s) of the dye, is maximised. Since essentially no fixation takes place at this pH, it is reasonable to surmise that this (high concentration of non-protonated nucleophilic amino groups) would be more than counteracted by the net electrostatic repulsion between highly anionic dye and anionic fibre. This is similar to the situation obtaining in reactive dyes for cellulose, where the electrostatic repulsion between anionic dye and negative



Fig. 2.

Table 4
(K/S)₁, (K/S)₂, % E and % T of dyes at pH 4

| Dye | | 0.05 | 0.1 | 0.2 | 0.5 | 0.8 | 1 | 1.5 | 2 |
|-----------------------------------|------------------------|------|------|------|------|------|------|-------|-------|
| Procion Red P-8B (D1) | (K/S) ₁ | 0.58 | 1.1 | 1.98 | 5.1 | 7.6 | 9.8 | 14.7 | 19.1 |
| | (K/S) ₂ | 0.55 | 1.02 | 1.83 | 4.64 | 6.38 | 7.9 | 10.7 | 11.26 |
| | % E | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | % T | 94 | 93 | 92 | 91 | 84 | 81 | 73 | 59 |
| Drimarene Red P-4B (D2) | (K/S) ₁ | 0.49 | 0.95 | 1.86 | 4.5 | 7.1 | 8.83 | 12.67 | 15.5 |
| | (K/S) ₂ | 0.46 | 0.85 | 1.38 | 3.06 | 4.13 | 4.43 | 5.16 | 5.28 |
| | % E | 100 | 100 | 100 | 100 | 97 | 96 | 90 | 79 |
| | % T | 94 | 89 | 74 | 68 | 56 | 48 | 37 | 27 |
| Procion Red H-EXL (D3) | (K/S) ₁ | 0.73 | 1.19 | 2.27 | 5.9 | 9.3 | 11.3 | 16.9 | 21.6 |
| | (K/S) ₂ | 0.7 | 1.14 | 2.1 | 5.13 | 7.9 | 9.49 | 12.33 | 14.39 |
| | % E | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | % T | 96 | 95 | 92.5 | 87 | 85 | 84 | 73 | 66 |
| Procion Red H-E7B (D4) | (K/S) ₁ | 0.57 | 1.12 | 1.64 | 3.94 | 4.9 | 5.9 | 7.1 | |
| | (K/S) ₂ | 0.56 | 0.99 | 1.6 | 3.4 | 4.5 | 5.15 | 6 | |
| | % E | 100 | 100 | 75 | 71 | 56 | 52 | 40 | |
| | % T | 98 | 88 | 73 | 61 | 51 | 45 | 34 | |
| Procion Red H-E3B (D5) | (K/S) ₁ | 0.52 | 1 | 1.96 | 4.31 | 6.85 | 8.9 | 12.38 | 14.7 |
| | (K/S) ₂ | 0.5 | 0.96 | 1.86 | 4.17 | 6.71 | 8.25 | 11.9 | 13.4 |
| | % E | 100 | 100 | 100 | 97 | 90 | 89 | 83.5 | 73 |
| | % T | 96 | 96 | 94.8 | 93.8 | 88 | 82.5 | 80 | 66.5 |
| Kayacelon React Red CN-3B (D6) | (K/S) ₁ | 0.41 | 0.69 | 1.19 | 2.2 | 2.56 | 2.75 | 3.51 | 3.82 |
| | (K/S) ₂ | 0.4 | 0.63 | 1.07 | 1.77 | 2.08 | 2.4 | 2.9 | 3.35 |
| | % E | 77.5 | 65 | 56 | 45 | 30 | 26 | 22 | 18 |
| | % T | 75 | 59 | 50.3 | 36 | 24 | 22 | 18 | 15.7 |
| Procion Rubine XL+ (D7) | (K/S) ₁ | 0.85 | 1.67 | 2.39 | 5 | 6.5 | 7.6 | 8.9 | 9.7 |
| | (K/S) ₂ | 0.62 | 0.9 | 1.6 | 3.2 | 4.26 | 4.75 | 5.4 | 5.7 |
| | % E | 100 | 100 | 73.5 | 60 | 50 | 48 | 36 | 28 |
| | % T | 72.9 | 54 | 50 | 39 | 32 | 30 | 22 | 16.4 |

fibre is reduced by addition of an electrolyte, such as common salt.

The protonation of the terminal amino end groups is an equilibrium process (Fig. 2).

In the presence of water, and depending on the pH within the fibre, the amino and carboxylic acid groups will be ionised to a greater or lesser extent. After the fibre is immersed in water the actual concentrations of the four possible fibre species [PA-NH₂, PA-NH₃⁺, PA-COOH, and PA-COO⁻, (PA- stands for the polyamide fibre backbone)] will depend on the original concentration of the available amino, and carboxylic acid groups, as well as the pH.

Table 5
Effective agent contents of dyes

| Dye | Molecular weight (MW) | Mol. In (MI) | Strength (%) |
|---------------------|-----------------------|--------------|--------------|
| Procion Red P-8B | 992 | 1824 | 54 |
| Drimarene Red P-4B | 851 | 1291 | 66 |
| Procion Red H-EXL | 890 | 1580 | 56 |
| Procion Red H-E7B | 1645 | 3715 | 44 |
| Procion Red H-E3B | 1341 | 2407 | 56 |
| Kayacelon React Red | 1560 | 4638 | 34 |
| Procion Rubine XL+ | 2341 | 3347 | 70 |

As all the dyes used in this study carry sulphonate groups, the observed increase in initial dye uptake (K/S value) that accompanied a decrease in pH of application can be attributed to a corresponding increase in ion–ion attractive interaction operating between the anionic sulphonate groups of the dye and the cationic protonated amino end groups of the nylon. Additionally, anionic carboxylate groups attached to the fibre will become protonated, thus reducing the electrostatic repulsion between the nylon and anionic dye. Consequently, pH is one of the key parameters influencing the level of exhaustion, and therefore final fixation, of reactive dyes to nylon.

Table 3 shows the colour strength (K/S value) and total fixation (% T) of 1% dye o.m.f for the dyes applied at different pH values. (K/S)₂ and % T were not determined in cases where exhaustion was extremely low.

When the pH is very low the concentration of NH₂ reduces even further and little fixation is observed. Additionally if the temperature is too high at low pH, polyamide hydrolysis is possible.

Generally the optimum pH for dyeing “Tactel Coloursafe” with the anionic reactive dyes examined was found to be around pH 4, at which pH reasonable to good dye exhaustion and fixation were achieved.

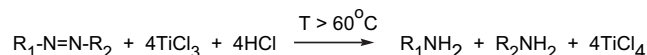


Fig. 3.

However, the optimum pH for dyeing varied slightly from dye to dye.

4.2. Build-up properties of dyes

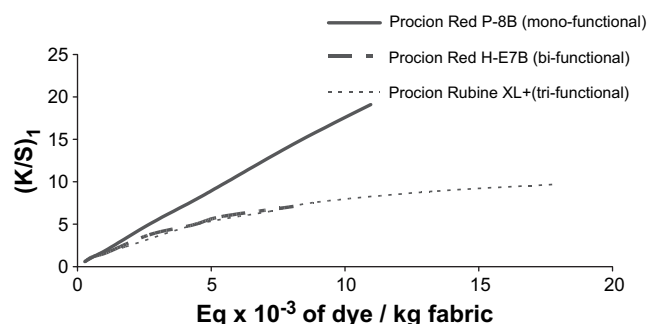
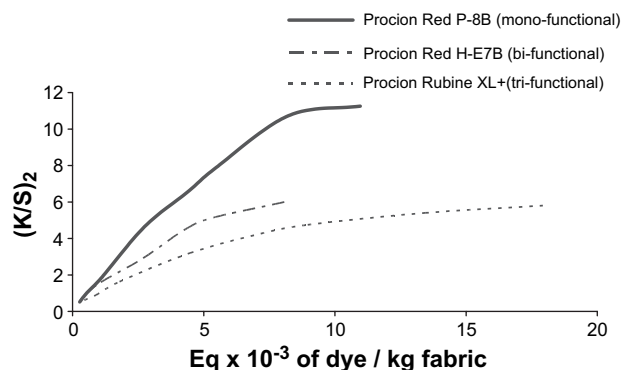
Having established that the optimum pH for dyeing is 4, the build-up properties of the dyes were examined using the dyeing application conditions shown in Fig. 1.

Table 4 lists the colour strength values (K/S) for each of the dyes, at pH 4, at a series of different concentrations of applied dye. (K/S)₁ refers to the observed colour strength before extraction with pyridine, (K/S)₂ refers to the colour strength after removal of any non-covalent bond by aqueous pyridine extraction.

4.3. Effect of varying the molecular size and the number of reactive groups

In order to make interpretation of results easier, and more meaningful, the effective agent content of each of the dyes was determined, by titration against titanium (III) chloride (Table 5). This allowed a direct comparison of equimolar quantities of dye on fabric. Additionally, because some of the dyes were di- or trimeric, the concentration of dye applied to fabric was always assessed using milli equivalents of dye. Thus complications arising from different effective agent contents and levels of functionality (mono-, di- or trimeric) were obviated.

The strength of the dyes were determined by titration with titanium (III) chloride [19–21] which causes reduction of the azo group with consequent discharge of colour. Results are shown in Table 5. Nowadays, the titrimetric estimation of azo dyes with titanous chloride is widely used to determine the purity of azo dyes. Under acidic conditions, titanous chloride reduces azo

Fig. 4. (K/S)₁ values of mono-, bi- and tri-functional dyes.Fig. 5. (K/S)₂ (fixed dye) values of dyes of mono-, bi- and tri-functional dyes.

linkages producing the corresponding amines as shown in Fig. 3.

The Mol. In (MI) represents the quantity of isolated dye (which contains water and electrolyte), in grams, which contains 1 mol of “pure” dye. This was determined from Eq. (4).

$$MI = \frac{\text{Mass} \times Hf \times 10,000}{Tf \times Vol} \quad (4)$$

where

Mass = the mass (g) of the impure dye.

Hf = the hydrogen factor which is the number of “hydrogens” required to reduce the azo or the nitro group, and is 4 and 6, respectively.

Tf = the titration factor which represents the strength ($Tf \leq 1$) of the titanous chloride solution and is determined by titration against a standard dye of a known MI (Procion Orange MX).

Vol = the volume (ml) of the titanous chloride solution required to reduce all the amount of the dye solution.

Because titanous chloride is readily oxidized by atmospheric oxygen, it was kept in a closed vessel under an inert atmosphere. The titration factor was determined

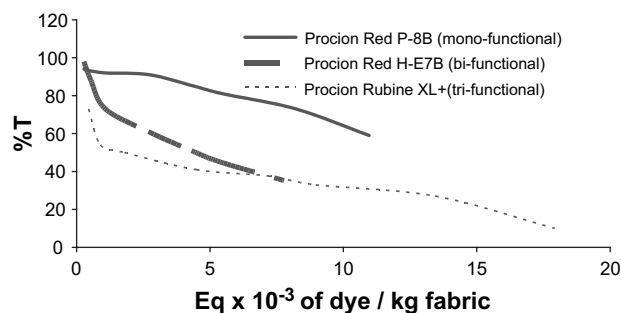


Fig. 6. % Fixation (%T) values of dyes of mono-, bi- and tri-functional dyes.

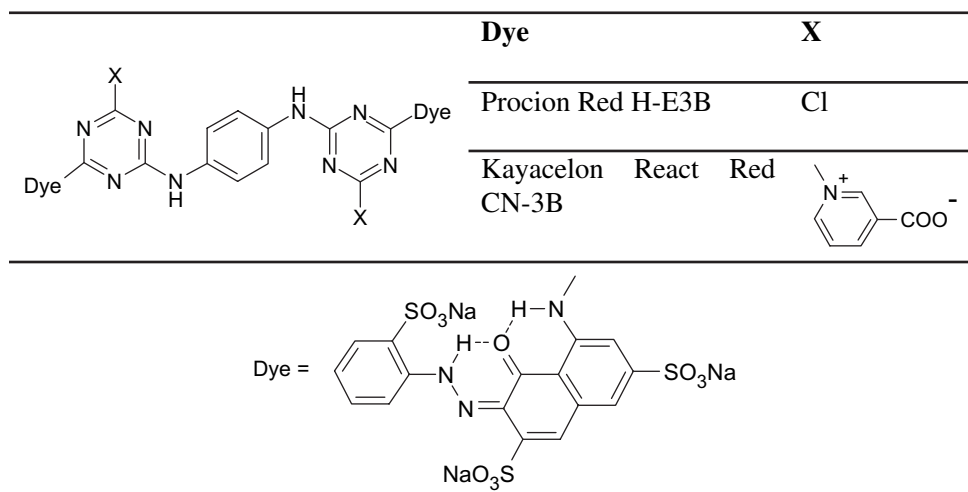


Fig. 7.

each time the titanium chloride is used. The discharge of dye colour indicated the end-point of the titration. Once the MI of the dye had been determined, its purity or, effective agent (EA) strength was determined (Eq. (5)).

$$EA = \frac{\text{Molecular weight}}{\text{MI}} \times 100\% \quad (5)$$

In order to gain some insight into the influence of the number of reactive groups on the dyeing of modified nylon three dyes, Procione Red P-8B (monochlorotriazinyl), Procione Red H-E7B (bis-monochlorotriazinyl) and Procione Rubine XL+ (tris-monochlorotriazinyl), were compared. All are based upon a similar chromophore, being derived from a sulphonated 2-aminonaphthalene, (diazo component) and H-acid, (coupling compound).

The initial exhaustion of the dyes varied markedly. Procione Red P-8B exhibited essentially complete exhaustion at all depths of applied dye (Table 5). This resulted in an almost linear increase in $(K/S)_1$ with increasing concentration of dye applied, suggesting that,

at least in pale to medium depths of shade, the Kebulka–Munk linear relationship of (K/S) with dye concentration [dye] was approximately valid. In contrast, the bi-functional dye, Procione Red H-E7B, and the tri-functional derivative, Procione Rubine XL+, exhausted completely only at very pale depths of shade, and thereafter exhaustion tailed off markedly. This might be associated with the larger size of the latter two dyes or their molecular shape. In the case of all of the dyes the $(K/S)_2$ values at the palest depths of shade, were very marginally less than the $(K/S)_1$ values, indicating high fixation of exhausted dye. At heavier depths the $(K/S)_2$ values deviated more markedly from $(K/S)_1$ indicating reducing levels of fixation (Figs. 4–6).

As the molecular size increases the level of fixation reduces, especially at heavier concentrations of applied dye. This is, in some ways, unexpected, since one equivalent of fixed colour of the mono-functional dye Procione Red P-8B, might be expected to occupy twice of many reactive sites on the fabric as the bi-functional Procione Red H-E7B, and three times as many as the tri-functional Procione Rubine XL+. This in turn suggests

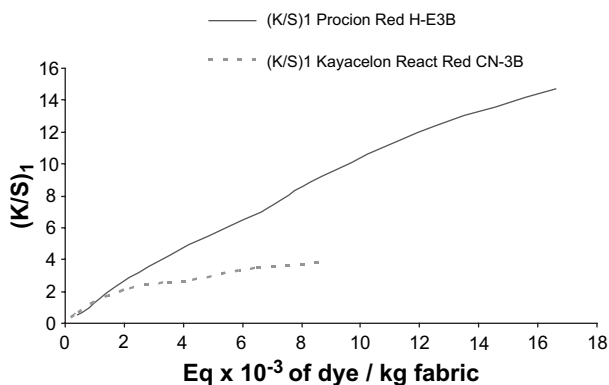


Fig. 8. Comparison of initial exhaustion, $(K/S)_1$, of Procione Red H-E3B with that of Kayacelon React Red CN-3B.

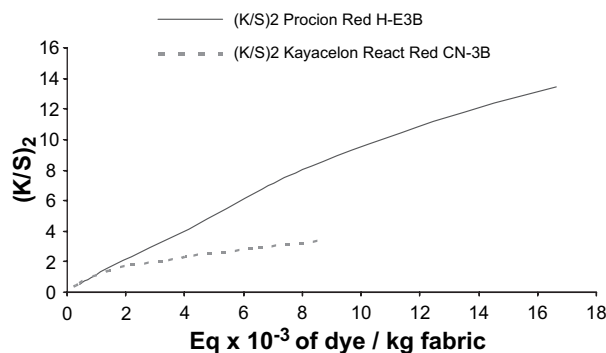


Fig. 9. Final exhaustion, $(K/S)_2$, of Procione Red H-E3B and Kayacelon React Red CN-3B.

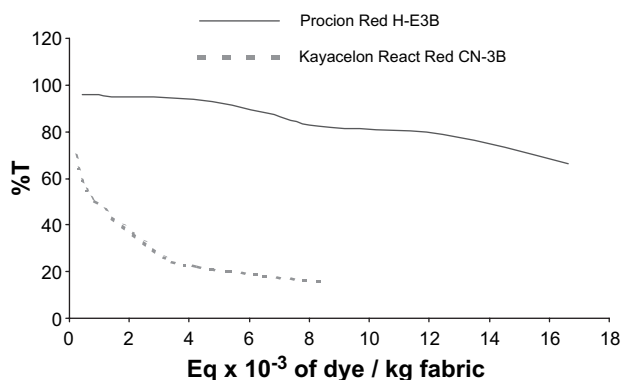


Fig. 10. Fixation of Procion Red H-E3B and Kayacelon React Red CN-3B.

that the formal availability of nucleophilic amino groups, per se, on the nylon is not the sole determinant of dye fixation.

4.4. Effect of changing the reactive group

Procion Red H-E3B and Kayacelon React Red CN-3B differ only in the nature of the reactive group, the former possessing two mono-chlorotriazine units and the latter two (3-carboxypyridinium) triazine units (Fig. 7). Indeed, Kayacelon React Red CN-3B dye is made by quaternisation of nicotinic acid with Procion Red H-E3B. The properties of these two dyes on nylon are compared in Figs. 8–10. The initial exhaustion, as measured by $(K/S)_1$ varies markedly (Fig. 8). This might appear surprising, since both have exactly the same chromophore and linking group, even the same net negative charge, assuming that the net negative charge associated with the 3-carboxypyridinium reactive group is zero.

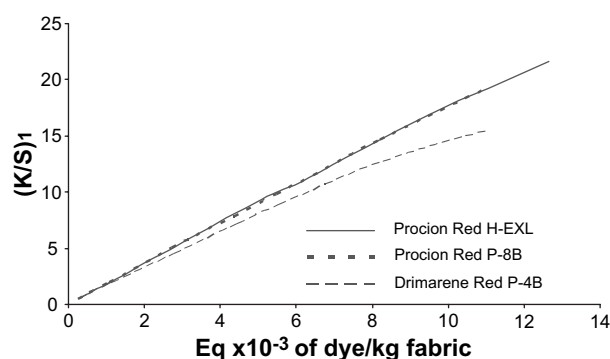


Fig. 12. Comparison of the initial exhaustion, $(K/S)_1$, value of Procion Red H-EXL with those of Procion Red P-8B and Drimarene Red P-4B.

4.5. Effect of changes in the “second leg” component attached to the triazine ring

In order to determine the influence of the number of sulphonic groups and the shape of the dye molecule on dyeing properties, three monofunctional monochlorotriazinyl cellulosic reactive dyes, Procion Red H-EXL, Procion Red P-8B and Drimarene Red P-4B (Fig. 11), were compared (Figs. 12–14). All were derived from 2-amino-naphthalene-1-sulphonic acid as diazo compound and H-acid as coupling compound, but the “second leg” substituent attached to the monochlorotriazinyl reactive group was varied.

All three dyes possess a single monochlorotriazinyl reactive group. The two Procion dyes, Procion Red H-EXL and Procion Red P-8B differ in the levels of sulphonation but behave very similarly in terms of initial exhaustion and fixation, suggesting that the degree of sulphonation may not always be an important determinant of dye fixation and build-up. Procion Red P-8B possesses four sulphonic acid groups and one

| Dye | R | X | Y |
|--------------------|-------------------------------|---------|----------------------|
| Procion Red P-8B | H | 2-COONa | 5-SO ₃ Na |
| Procion Red H-EXL | H | 4-COONa | H |
| Drimarene Red P-4B | C ₂ H ₅ | H | H |

Dye

Dye=

Fig. 11.

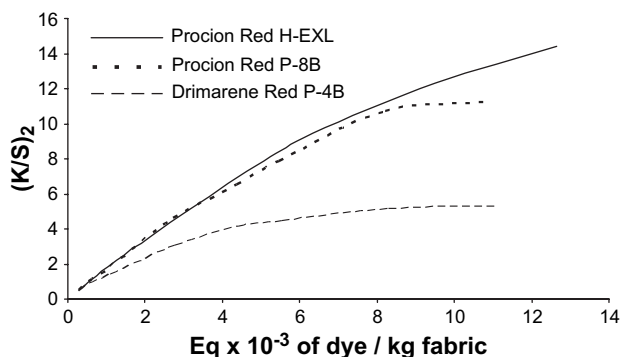


Fig. 13. Comparison of the final exhaustion, $(K/S)_2$, value of Procion Red H-EXL with those of Procion Red P-8B and Drimarene Red P-4B.

carboxylic acid group whereas Procion Red H-EXL possesses one less sulphonic acid group. Drimarene Red P-4B, like Procion Red H-EXL, is a trisulphonated dye but initial exhaustion and fixation are both far inferior to the other two dyes, suggesting that, at least in this case, the shape of the molecule may be more important in determining dyeing properties on modified nylon 6.6. The introduction of an *N*-alkylarylamine as a “second leg” component is a well known route to highly soluble, low substantive dyes for printing of cellulosic substrates, this high solubility is generally believed to be attributable to the molecule being non-planar, the plane of the “second leg” being at a large dihedral angle to the rest of the molecule.

This concept was further investigated when the three-dimensional (auto optimisation) structures were computed using HyperChem, version 7.5 software. These three-dimensional images suggested that in Procion Red P-8B and Procion Red H-EXL the arylamine substituent and triazine rings were closer to being coplanar than in Drimarene Red P-4B, where the triazine and arylamine substituents ring deviate much more markedly from coplanarity. This deviation from coplanarity of the molecule allows less interaction of dye with fibre surface and this is probably responsible for lowering of dye uptake, and hence, exhaustion and fixation of Drimarene Red P-4B.

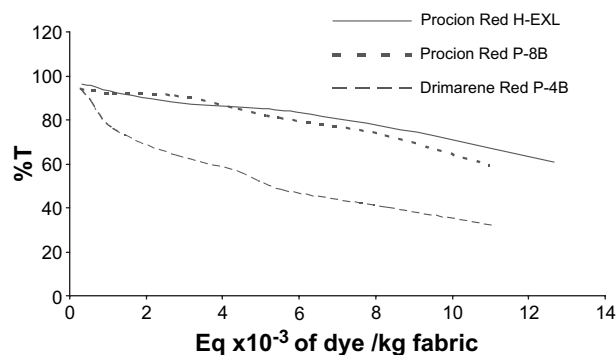


Fig. 14. Comparison of the total fixation, $\%T$ value of Procion Red H-EXL with those of Procion Red P-8B and Drimarene Red P-4B.

4.6. Wash fastness properties of dyes

The wash fastness properties of dyes were assessed using the ISO 105CO6/C2S at 60 °C wash fastness test protocol [22]. The change in shade and the degree of cross staining were assessed visually using grey scales and the results are presented in Table 6.

Wash fastness of each dye fixed to nylon 6.6 fabric was very good, at every depth of shade employed.

5. Conclusions

- In dyeing of *Tactel Coloursafe* with anionic reactive dyes, the optimum pH of application is 4. At this pH, the rate of hydrolysis of the electrophilic reactive groups, by water, will be much lower than the rate of hydrolysis of cellulose reactive dyes, by hydroxide, at high pH.
- As the number of reactive groups increases, the colour yield and fixation decreases.
- The chlorotriazine reactive group is more fixation efficient on nylon than the 3-carboxypyridinium triazine reactive groups.
- The degree of dye sulphonation is not always an important determinant of dye fixation and build-up on nylon. The shape and size of the molecules is more important in determining dyeing properties on nylon.

Table 6
Wash fastness results of dyes in the ISO 105CO6/C2S

| Dye | Staining | | | | | |
|--------------------|-----------------------------|--------------------------|-----------|-----------|---------|------|
| | Secondary cellulose acetate | Bleached Un-merc. cotton | Nylon 6.6 | Polyester | Acrylic | Wool |
| Procion Red P-8B | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 |
| Procion Red H-EXL | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 |
| Drimarene Red P-4B | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 |
| Procion Red H-E7B | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 |
| Procion Red H-E3B | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 |
| Procion Rubine XL+ | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 |

Acknowledgement

We wish to express our gratitude to UMIST and to Professor D. A. S. Phillips for financial support (to A. S.-G.).

References

- [1] Burkinshaw SM. Chemical principles of synthetic fibre dyeing. London: Chapman & Hall; 1995.
- [2] Stephen WE. GB785120-1957-10-23.
- [3] Stephen WE. GB785222-1957-10-23.
- [4] Rattee I. GB797946-1958-07-09.
- [5] Rattee I. GB798121-1958-07-16.
- [6] Stead CV. In: Shore J, editor. Colorants and auxiliaries. Bradford: Society of Dyers and Colourists; 1990.
- [7] Fox MR, Summer HH. In: Preston C, editor. The dyeing of cellulosic fibres. Bradford: Dyers Company Publication Trust; 1986.
- [8] Renfrew AHM. Reactive dyes for textile fibres. Bradford: Society of Dyers and Colorists; 1999.
- [9] Ginns P, Silkstone K. In: Nunn DM, editor. The dyeing of synthetic – polymer and acetate fibres. The Dyers Company Publications Trust; 1979.
- [10] Lewis DM. In: Lewis DM, editor. Wool dyeing. Bradford: Society of Dyers and Colourists; 1992.
- [11] DyStar. USP 5, 803, 930; 1998.
- [12] Ciba. www.cibasc.com.
- [13] Burkinshaw SM, Gandhi K. The dyeing of conventional decitex and microfibre nylon 6,6 with reactive dyes – 1. Chlorodifluoropyrimidinyl dyes. *Dyes Pigments* 1996;32:101.
- [14] Burkinshaw SM, Gandhi K. The dyeing of conventional and microfibre nylon 6,6 with reactive dyes – 2. α -Bromoacrylamido dyes. *Dyes Pigments* 1997;33:259.
- [15] Burkinshaw SM, Wills AE. The dyeing of conventional and microfibre nylon 6,6 with reactive dyes – 3. Vinyl sulphone and chlorotriazine dyes. *Dyes Pigments* 1997;34:243.
- [16] Burkinshaw SM, Son Young-A, Bide MJ. The application of hetero bi-functional reactive dyes to nylon 6,6: process modifications to achieve high efficiencies. *Dyes Pigments* 2001;48:245.
- [17] Burkinshaw SM, Collines GW. *Dyes Pigments* 1994;25:31.
- [18] Vogel A. A textbook of quantitative inorganic analysis. London: Longmans; 1944.
- [19] Knecht E, Hibbert E. New reduction methods in volumetric analysis. London: Longmans, Green and Co.; 1925.
- [20] Giles CH, Grezek J. *Textile Research Journal* 1962;7:509.
- [21] Venkataraman K. In: The chemistry of synthetic dyes, vol. II. New York: Academic Press Inc.; 1952. p. 1345.
- [22] Society of Dyers and Colourist. Standard methods for the determination of the colour fastness of textiles and leather. 5th ed. Bradford, UK: Society of Dyers and Colourist; 1990.